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AUTHOR(S):

KOBAYASHI, Mei; RABITZ, Herschel; YETTER, Richard

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Direct Inversion of a 28-step CO-hydrogen-oxygen Reaction Mechanism

Mei KOBAYASHI ¹, Herschel RABITZ ² and Richard YETTER ³

mei@trlvm.vnet.ibm.com, hrabitz@chemvax.princeton.edu

rich@pyros.princeton.edu

This paper presents results from the numerical implementation of an algorithm for the direction inversion of data to yield unknowns [2] to study inverse problems associated with a 28-step CO-hydrogen-oxygen reaction mechanism proposed in [10]. In section 1, we describe the class of chemical inverse problems which are suitable for study using the technique. The algorithm and examples of applications are given in section 2. Results from our investigation of a CO-hydrogen-oxygen reaction mechanism will be described in the final section.

1. Introduction and Problem Formulation

The problem considered in this paper lies in a very active area of research known as inverse problems. All inverse problems are associated with a forward problem, which is often much easier to solve. For example, consider a simple system studied by Euler and Bernoulli: given the density, length and tension of a plucked string, determine the tones produced. An associated inverse problem is to determine the density of the string from its tones, length and tension [3]. Inverse problems appear in a wide range of scientific areas which include: the reconstruction of images in X-ray tomography, the study of potential flows and heat conduction, the determination of material properties of a beam from its vibrational modes, the recovery of a cross-sectional area of the vocal tract from measured data, the determination of the density inside the earth from seismographic data, and mathematical inverse problems.

The main topic of this paper is an inverse problem which arises in the field of chemical kinetics. Kinetics systems are often described by evolution-type equations of the form:

$$\frac{\partial u}{\partial t} = T(V, u(V)) \quad \text{for } t > 0, \quad (1)$$

$$u = u_0 \quad \text{for } t = 0, \quad (2)$$

where u is a vector representing the concentration of chemical species and V describes other parameters, e.g., diffusion and kinetics rate constants [1]. The standard textbook

¹IBM Tokyo Research Laboratory, 1623-14, Shimotsuruma, Yamato-shi, Kanagawa-ken 242 Japan.

²Dept of Chemistry, Princeton Univ., Princeton, New Jersey 08544 U.S.A..

³Dept. of Mechanical & Aerospace Eng., Princeton Univ., Princeton, New Jersey 08544 U.S.A..

or *forward* problem consists of determining u for a choice of V . In actual laboratory situations some of the V_i may not be measurable, even though we would like accurate approximations of their values under various conditions, e.g. temperature, pressure. This quandary may be formulated as a mathematical *inverse* problem; determine V , given a set of data measurements $d = \{d_j\}$, which are related to V through equations of the form:

$$L_j(u, V) = f_j(d_j, u) ; \quad j = 1, 2, 3, \dots, m , \quad (3)$$

where each $L_j(u, V)$ is a, possibly non-linear, operator acting on u and V . An algorithm for determining a numerical solution to this problem is given in the next section.

2. Algorithm and Examples

An algorithm proposed by Caudill, Rabitz and Askar [2] for the direct inversion of data to yield unknown functions consists of three steps:

- (i) Formally invert the system (3) to express the unknown V in terms of the data d and the (unknown) forward solution u :

$$V = \nu[d, u] . \quad (4)$$

- (ii) Input (4) into equation (1) and solve the resulting system for u .
- (iii) Substitute the solution u obtained in step (ii) into the right-hand-side of (4) to determine V explicitly in terms of the data d .

Since the algorithm is based on system identities, it should be of no surprise if it yields excellent results for clean and complete data sets. Through implementation studies, we seek to determine its ability to reconstruct desired parameters from ideal as well as incomplete or noisy laboratory data.

This algorithm can be used to solve a variety of inverse problems which can be mathematically modeled by equations of the form (1)–(2) with measurable laboratory data (3). Three other types of applications: heat conduction, age-structured population dynamics and molecular dynamics are discussed in [2].

3. Numerical Experiments

In this section we describe results from the implementation of the algorithm from section 2 to solve the inverse problem for recovery of kinetics rate constants for a non-linear, highly coupled 28-step reaction mechanism for the oxidation of carbon monoxide in

the presence of hydrogen proposed by Yetter, Dryer and Rabitz in [10]. Before considering this complicated system, we examined the simple explosive reaction model



as a feasibility study. Here the forward and backward rate constants for the propagation and termination reactions are k_1 , k_2 , k_3 , and k_4 respectively [8]. We assume that an infinite reservoir of the principal reagent is available and no or negligible back reactions take place. Our numerical experiments consisted of 4 steps:

1. Given all rate constants and initial concentrations of all reagents, solve the forward problem, i.e. determine concentrations of all reagents for finite times $t : 0 \leq t < \infty$.
2. Select data for concentrations of reagents at various times $0 = t_0 < t_1 < \dots < t_n$.
3. Formulate the inverse problem and apply the algorithm from section 2.
4. Compare the computed algorithm from step 3 with the actual solution from step 1.

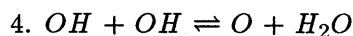
A basic forward difference scheme was used to solve the forward problem, i.e., compute the concentrations of X , A and B . Subsets of the generated data were used to solve an inverse problem. We considered the inverse problem: Given the rate constants k_1 , k_{-1} , k_{-2} and the concentrations of A and B , determine the concentration of X and the rate constant k_2 . Recovery of both was perfect (within significant digits), even when partial data sets were used.

The 28-step CO-Hydrogen-Oxygen reaction mechanism we considered is given below [10]. Although the mechanism has been validated for a wide range of conditions, the regions of calibration may differ quite a bit from step to step. One of the motivations for our work is to examine the reaction mechanism under a range of conditions, some of which may not be experimentally validated. A second motivation is the study of the sensitivities of the reagents and rate constants to changes in experimental conditions.

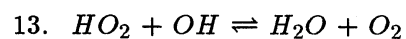
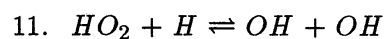
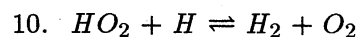
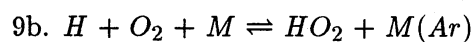
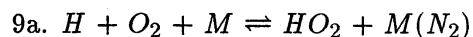
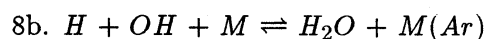
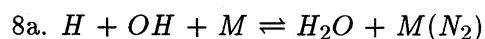
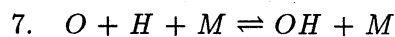
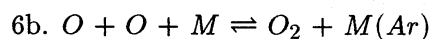
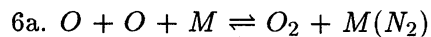
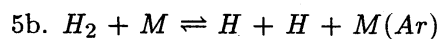
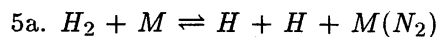
CO, H₂, O₂ Reaction Mechanism

H₂, O₂ Chain Reactions

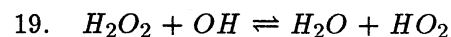
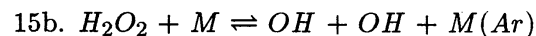
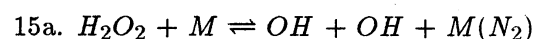
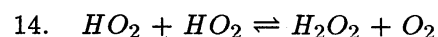
1. $H + O_2 \rightleftharpoons O + OH$
2. $O + H_2 \rightleftharpoons H + OH$
3. $OH + H_2 \rightleftharpoons H + H_2O$



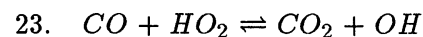
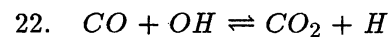
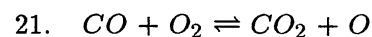
H_2 , O_2 Dissociation-Recombination Reactions



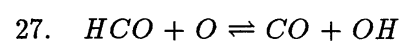
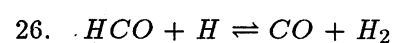
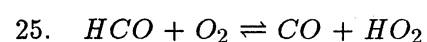
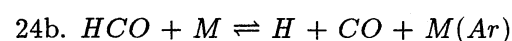
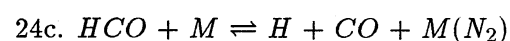
Formation and Consumption of H_2O_2



Oxidation of CO



Formation and Consumption of HCO



Forward and backward rate constants for the reactions were computed using data from [5],[7],[10] and the *Arrhenius rate formula* $k = AT^n \exp(-E_a/RT)$, where A is the *pre-exponential factor* (which is independent of temperature, or nearly so), T is the *temperature*, n a power index, E_a the *activation energy*, and R the *gas constant*. For reactions 4 and 22, we use the formulae $k_4 = 5.46 \times 10^{11} \exp(0.00149 \times T)$ and $k_{22} = 6.75 \times 10^{10} \exp(0.000907 \times T)$ given in table III of [10] in lieu of the values for A , n and E_a .⁴ Even when temperatures selected for study do not necessarily fall within the calibration range given in the table, we use them as a best estimate.

We follow step 1 of the procedure outlined for the study of the explosive kinetics model and simulate the forward problem. Since this system is very stiff, a simple finite difference scheme will lead to poor results [6]; a backward Euler method, such as the LSODE package of Hindmarsh [4] yields good results for small temporal meshsizes. Our studies use the same initial conditions as those in a series of sensitivity analysis experiments in figure 7, p. 115 of [10], in which results from numerical simulations were verified with shock tube experimental data. The initial conditions are: $[CO] = 0.0093$, $[O_2] = 0.0105$, $[H_2O] = 0.0058$, $[N_2] = 0.9744$, $T = 1033K$, and $P = 1$ atm, where all concentrations are in mole fractions. Initial concentrations of all other reagents are zero. In running LSODE, we set $t = 0$, $tt = tout = 0.1d-11$, $itol = 2$, $rtol = atol = 1.0d-10$ (for all reagents), $itask = 1$, $istate = 1$, $iopt = 0$, $lrw = 250$, $liw = 31$, and $mf = 21$.

There are several possible ways to recover a rate constant for a particular reaction from the concentrations of all species and other rate constants; Inversion of the rate equation for any of the species involved in the reaction can be used. For example, consider the problem of recovering the constant, k_{22} , for the twenty second reaction, which involves four species (H , OH , CO and CO_2). We demonstrate the inversion process using the rate equation for CO_2 .

$$\begin{aligned} \frac{\partial[CO_2]}{\partial t} = & k_{20}[CO][O][N_2] - k_{-20}[CO_2][N_2] + k_{21}[CO][O_2] - k_{-21}[CO_2][O] \\ & + k_{22}[CO][OH] - k_{-22}[CO_2][H] + k_{23}[CO][HO_2] - k_{-23}[CO_2][OH] \end{aligned}$$

A forward differencing scheme for $\partial[CO_2]/\partial t$ is used to solve for k_{22} , because it is the simplest tool for solving our problem, however, we note two drawbacks of forward differencing: first, LSODE uses backward differences (which means that we are combining two

⁴There are different ways to compute backward rate constants, but the method given above appears to be the best. Another method, which relies on the thermodynamic equations: $\Delta H(T) = \Delta H(298.15) + \int_{298.15}^T c_p(\tau) d\tau$, $\Delta S(T) = \Delta S(298.15) + \int_{298.15}^T (c_p(\tau)/\tau) d\tau$, $\Delta G(T) = \Delta H(T) - T\Delta S(T)$, and $k_r = k_f \exp(-\Delta G/RT)$, yields considerably different rate constants, which lead to poor simulation results. Errors from computation of the exponential term may be the cause.

inconsistent schemes), and second, forward differencing is inherently less stable (which was our motivation for choosing LSODE). In light of the above, we are careful to select extremely small step sizes when using the solution formula

$$\begin{aligned}
 k_{22}[CO]_i[OH]_i = & \frac{-[CO_2]_{i+1} + [CO_2]_i}{\Delta t} - k_{20}[CO]_i[O]_i[N_2]_i - k_{-20}[CO_2]_i[N_2]_i \\
 & - k_{21}[CO]_i[O_2]_i - k_{-21}[CO_2]_i[O]_i \\
 & + k_{-22}[CO_2]_i[H]_i - k_{23}[CO]_i[HO_2]_i - k_{-23}[CO_2]_i[OH]_i .
 \end{aligned}$$

The subindices i and $i+1$ indicate data from the i^{th} and $(i+1)^{th}$ timestep should be used. Recovery of k_{22} is perfect within the number of significant digits of the initial data used in computations, as can be seen in the first figure in the appendix. When a backward differencing scheme is used, convergence to the correct value for k_{22} is faster, but results are the same after a short while, as shown in the second figure. An analogous procedure can be used to determine k_{22} by inverting any one of the other rate equations. Results from using the rate equation for hydrogen, $\partial[H]/\partial t$, and carbon monoxide, $\partial[CO]/\partial t$ are given in the third and fourth figures in the appendix.

The technique used to determine k_{22} can be used to solve analogous problems for the recovery of other rate constants. The chart in the appendix indicates (with a circle mark) which rate constants can, in principle, be determined from which rate equation. The horizontal labels are for the rate equations, the vertical for the reaction number. We are currently investigating formulations of other solvable inverse problems, including those in which only noisy and incomplete data are available.

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The chart below indicates (with a circle mark) which rate constants can, in principle, be determined from which rate equation. The horizontal labels are for the rate equations, the vertical for the reaction number.

rxn	H	O	OH	H2	O2	H2O	HO2	H2O2	CO	CO2	HCO
1	o	o	o		o						
2	o	o	o	o							
3	o		o	o		o					
4		o	o			o					
5	o			o							
6		o			o						
7	o	o	o								
8	o		o			o					
9	o				o		o				
10	o			o	o		o				
11	o		o				o				
12		o	o		o		o				
13			o		o	o	o				
14					o		o	o			
15			o					o			
16	o		o			o		o			
17	o			o			o	o			
18		o	o				o	o			
19			o			o	o	o			
20		o							o	o	
21		o			o				o	o	
22	o		o						o	o	
23			o				o		o	o	
24	o								o		o
25					o		o		o		o
26	o			o					o		o
27		o	o						o		o
28			o			o			o		o

